

Microscale Characterization of the Location and Association of TNT in Soils

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INTRODUCTION:

Numerous ammunition manufacturing facilities and ammunition testing sites across the world are faced with environmental problems associated with soils contaminated with trinitrotoluene (TNT) and other nitroaromatic compounds. Although a number of TNT treatment technologies have been developed recently [1,2], these techniques do not result in a high degree of mineralization of the explosive compounds present. Thus, a significant part of the contaminant mass remains in the soil as residues of the original contamination. The acceptance of cost-effective treatment techniques depends on better understanding of the stabilization of TNT and its nitroaromatic transformation products in soil. The chemical and biological availability of TNT residues in soil is determined primarily by the physical and chemical form in which TNT remain in soils. Reduction of TNT produces aminonitrotoluenes, which may covalently bond irreversibly with quinones, and reversibly with hydroquinones. Such transformation of molecular structure is implicated in making TNT transformation products unavailable for further degradation [3]. However, TNT residue may also be present in a solid form in soils, especially at former production facilities. Solid TNT particles may create a toxic zone in the vicinity thereby making biodegradation difficult. Thus it is important to understand the microscale nature of TNT residues found in contaminated soils.

In our previous work, microscale analytic techniques were used successfully to demonstrate the preferential binding of polycyclic aromatic hydrocarbons (PAHs) on coal-derived particles in sediment [4,5]. We showed in that work that PAH sorption on coal-derived particles is associated with minimal biodegradation, slow release rates, and high desorption activation energies, while PAH sorption on clay/silt particles is associated with significant potential biodegradability, relatively fast release rates, and lower desorption activation energies.

The primary focus of the current work is to develop microscale analytic techniques to assess whether crystalline TNT may exist in impacted soils and to apply these techniques to determine whether the presence of crystalline or pure TNT in soil may explain differences in biotreatability of TNT-impacted soils from the field.

RESULTS AND DISCUSSION:

The focus of this research is to develop methods to permit the identification at the particle and sub-particle scale whether solid-phase, crystalline TNT, or crystalline TNT transformation products exists in field soils. Infrared spectromicroscopy available at beamline 1.4 was used to detect the presence of solid TNT in contaminated soils. Although the fate of TNT and its transformation products in soil has been the subject of numerous investigations, important questions remain on whether pure solid TNT may account for an untreatable fraction of TNT in field samples. The hypothesis is that crystalline or pure TNT is toxic to microorganisms and not easily biotreatable and that differences in biotreatment of TNT-impacted soil may depend on whether the TNT is present as sorbed versus solid, crystalline form. Soil samples were obtained from two ammunition manufacturing facilities. Soils from these field sites are currently being

tested for possible application of biotreatment technologies. Half a gram of each soil was spread on red clay mounted on a microscope slide. IR analysis was carried out in the reflectance mode. In our investigations using IR spectromicroscopy we observed the presence of significant quantities of residual crystalline TNT embedded in both soil samples. We could identify solid TNT based on the unique spectral characteristics of the nitro groups present in TNT. As shown in Figure 1, strong IR absorbance peaks near 1550 and 1350 wavenumbers are indicative of the asymmetric and symmetric stretch vibrations of the NO_2 groups present in the TNT molecules. To illustrate the physical location and form of the solid TNT particles, a representative soil agglomerate containing solid TNT was investigated for TNT presence using line scanning as shown in Figure 2. Multiple spots along a straight line through the TNT spot were analyzed in the IR spectromicroscope. As shown in Figure 2, the two absorbance peaks for the nitro groups show up when the scan passes through the TNT spot in the image shown on top. The rest of the soil barely shows any appreciable TNT signal. Thus, the residual TNT seems to be present predominantly in the solid particulate form. A light-microscope image of the solid TNT spot reveals a crystalline structure as shown in Figure 2. A unique finding in our work using IR spectromicroscopy is the direct measurement of residual crystalline TNT embedded in soil as opposed to TNT sorbed on mineral or organic matter. This finding of the microscale nature of TNT residuals in field materials has a major implication on its availability and toxicity. Current work in this research is investigating the effect of crystalline TNT on biological and chemical treatment methods. We are investigating the behavior of TNT degrading organisms near the vicinity of TNT crystals in soil using live-dead staining procedures and visualization through laser confocal microscopy. The results from the research will provide important information on the particle and sub-particle locations of solid, crystalline TNT and whether this accounts for the variability in biotreatment of TNT.

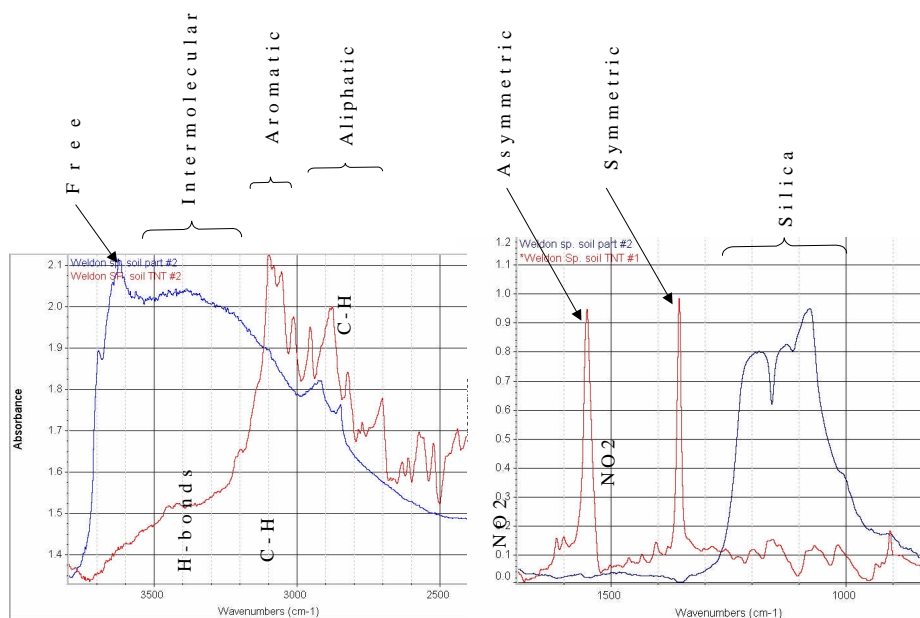


Figure 1. Results of experiments conducted at Beamline 1.4.2 illustrating the use of IR spectromicroscopy to identify the location of TNT micro-crystals present in contaminated soil from an ammunition manufacturing facility. The red line shows the absorbance spectra of the TNT crystal embedded in soil (blue line).

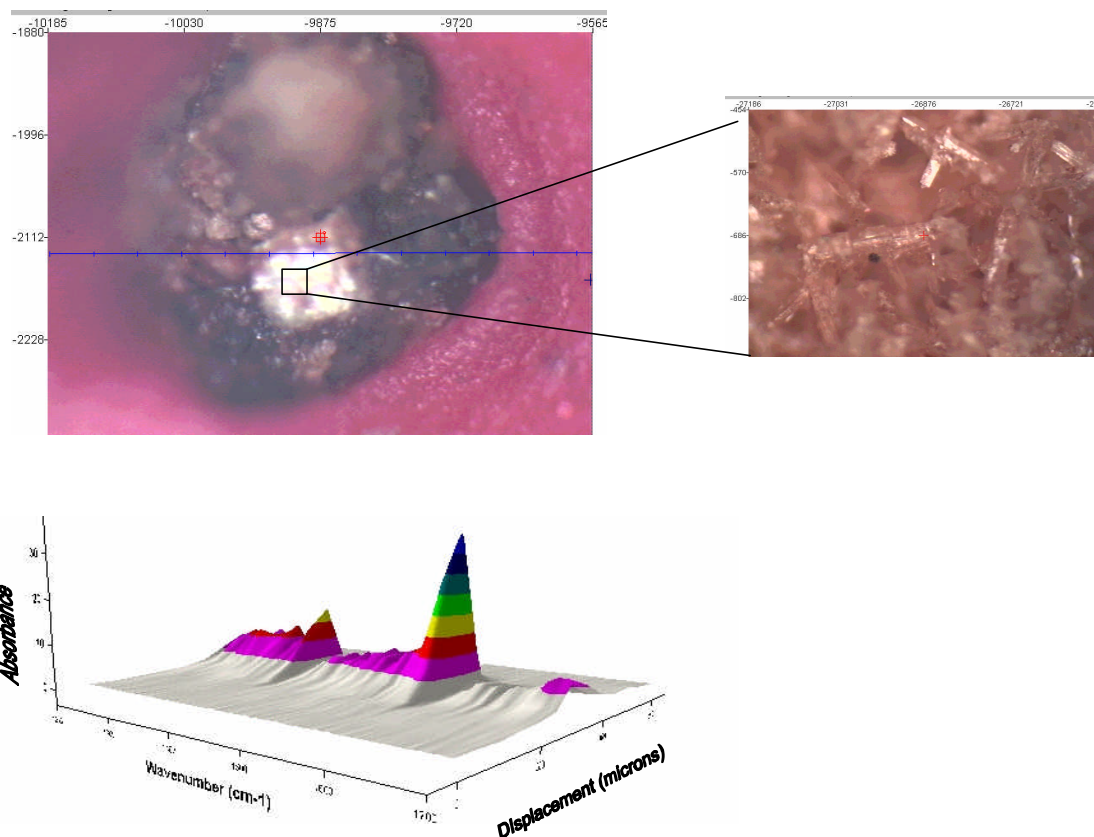


Figure 2. Top picture shows a soil particle with a white crystalline spot that was identified as crystalline TNT based on IR spectral map shown below. Contour map below shows IR absorbance along the blue line across the soil particle. The two prominent NO₂ stretch vibrations indicate a strong presence of TNT in the white spot. Image on the right shows a magnified image of the crystalline nature of TNT seen embed in the soil particle.

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Funding for this work was provided by the US Army Waterways Experiment Station, Vicksburg, MS.

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